

## Fundamental Discoveries in Heterogeneous Catalysis Focus Topic

Room 201A - Session HC+SS-WeM

### Mechanisms and Reaction Pathways of Heterogeneously Catalyzed Reactions

Moderator: Johan Gustafson, Lund University

8:00am **HC+SS-WeM-1 Surface Reactions of Methanol on Fe<sub>3</sub>O<sub>4</sub>(001) and Pd/Fe<sub>3</sub>O<sub>4</sub>(001) Model Catalysts**, *Matthew Marcinkowski, N Doudin, R Smith, B Kay, Z Dohnalek*, Pacific Northwest National Laboratory

Single atom catalysts offer potential improvements in reactivity, selectivity, and decreased catalyst cost, but are often difficult to characterize and stabilize. Iron oxides are frequently used as catalyst supports, and recent studies have shown that Fe<sub>3</sub>O<sub>4</sub>(001) magnetite can stabilize isolated atoms of many transition metals.<sup>1</sup> This property makes the (001) surface of magnetite ideal for model studies of the catalytic activity of supported single atoms. In this study, we examine the adsorption and reaction of methanol on Fe<sub>3</sub>O<sub>4</sub>(001) and Pd/Fe<sub>3</sub>O<sub>4</sub>(001) surfaces using a combination of scanning tunneling microscopy, temperature programmed desorption, and x-ray photoelectron spectroscopy. We find that a monolayer of methanol saturates on Fe<sub>3</sub>O<sub>4</sub>(001) at a coverage of  $5.8 \times 10^{14}$  molecules/cm<sup>2</sup>, which corresponds to one methanol per every surface Fe<sup>3+</sup> ion. The majority of methanol desorbs molecularly by 280 K. Above 300 K, methanol dissociates to form methoxy and hydroxyl species.<sup>2</sup> The maximum coverage of methoxy that can be achieved is  $1.2 \times 10^{14}$  molecules/cm<sup>2</sup>. The methoxy species form an ordered layer adsorbed on the Fe<sup>3+</sup> sites above the subsurface cation vacancies. At elevated temperatures, the methoxy species react via one of two processes: recombining with hydroxyl to desorb as additional molecular methanol at 350 K, or further dehydrogenation to produce formaldehyde above 500 K. Production of formaldehyde is limited to  $2.3 \times 10^{13}$  molecules/cm<sup>2</sup>. On single Pd atoms on Fe<sub>3</sub>O<sub>4</sub>(001), the production of formaldehyde above 500 K is suppressed while a new formaldehyde channel is observed at 300 K. Increasing the Pd atom concentration increases the magnitude of the low-temperature channel. Interestingly, the total amount of formaldehyde produced in these two channels remains constant throughout the range of Pd concentrations studied, indicating that the methoxy species are formed on the Fe<sub>3</sub>O<sub>4</sub> substrate and Pd atoms only facilitate the conversion of methoxy species to formaldehyde. However, the appearance of the lower temperature reaction channel for formaldehyde shows that the Pd atoms lower the reaction barrier to dehydrogenate methoxy to formaldehyde by almost a factor of two.

1. R. Bliem et al. *Phys. Rev B* **92**, 075440 (2015)

2. O. Gamba et al. *Top. Catal.* **60**, 420 (2017)

8:20am **HC+SS-WeM-2 Hydrogen Activation and Spillover on Single Palladium Atoms Supported on Fe<sub>3</sub>O<sub>4</sub>(001) Surface**, *Nassar Doudin*, Pacific Northwest National Laboratory; *J Cheng Liu*, Tsinghua University, China; *M Marcinkowski, M Nguyen*, Pacific Northwest National Laboratory; *J Li*, Tsinghua University, China; *V Glezakou*, Pacific Northwest National Laboratory; *G Parkinson*, Vienna University of Technology, Austria; *R Rousseau, Z Dohnalek*, Pacific Northwest National Laboratory

Single-atom catalysts have recently attracted great attention due to their ultimate metal efficiency and the promise of novel properties. However, at the atomic level, little is known about their stability, interactions with the support, and mechanisms by which they operate. Recently it has been shown that on Fe<sub>3</sub>O<sub>4</sub>(001) surface, single metal atoms can be stabilized to temperatures as high as 700 K [1]. This high stability makes Fe<sub>3</sub>O<sub>4</sub>(001) a promising support for model studies of single atom catalysts. Here, we present a room-temperature study of H<sub>2</sub> dissociation on single Pd atoms on Fe<sub>3</sub>O<sub>4</sub>(001) followed by H atom spillover via scanning tunneling microscopy (STM) and density functional theory (DFT). The exposure to H<sub>2</sub> at 300 K results in the appearance of bright double protrusions located on surface iron (Fe<sub>s</sub>) sites. Such protrusions were observed previously [2] following the adsorption of atomic H and hydroxyl formation (O<sub>s</sub>H) on bare Fe<sub>3</sub>O<sub>4</sub>(001). By analogy, we attribute the features observed here to O<sub>s</sub>H species. The DFT calculations further reveal that H<sub>2</sub> dissociates heterolytically and spills over both hydrogen atoms onto Fe<sub>3</sub>O<sub>4</sub>(001). When the exposure to H<sub>2</sub> is increased, the density of O<sub>s</sub>H's is also observed to increase. With approximately every fourth surface oxygen atom hydroxylated, many areas show a local order with O<sub>s</sub>H's spaced according to the (√2×√2)R45° surface reconstruction. STM data further indicate that H

atoms diffusion is accelerated in the presence of coadsorbed water. At highest coverages of O<sub>s</sub>H's (approximately every second oxygen atom hydroxylated), the reconstruction is lifted, and the Pd atoms become destabilized. These studies clearly demonstrate that single Pd atoms can efficiently dissociate H<sub>2</sub> that spills over onto a reducible oxide support that can be extensively hydroxylated.

[1] R. Bliem et al. *Science* **346**, 6214 (2014).

[2] G. S. Parkinson et al. *Phys. Rev. B* **82**, 125413 (2010).

8:40am **HC+SS-WeM-3 Model Studies on Ligand-assisted Heterogeneous Catalysis**, *Swetlana Schauerermann*, Christian-Albrechts-University Kiel, Germany **INVITED**

Identifying the surface processes governing the selectivity in hydrogenation of  $\alpha,\beta$ -unsaturated carbonyl compounds on late transition metals is crucial for the rational design of new catalytic materials with the desired selectivity towards C=O vs. C=C bond hydrogenation. In the present talk it will be shown that the selectivity of these reactions can crucially depend on the presence of specific ligand-like surface co-adsorbates. Specifically, I will present a mechanistic study on selective hydrogenation of acrolein over model Pd surfaces – both single crystal Pd(111) surface and Pd nanoparticles supported on a model oxide support.<sup>1</sup> We show for the first time that selective hydrogenation of the C=O bond in acrolein to form the desired reaction product – an unsaturated alcohol propenol – is possible over Pd(111) with nearly 100 % selectivity. However, this process requires a very distinct modification of the Pd(111) surface with an overlayer of oxopropyl spectator species that are formed from acrolein during the initial stages of reaction and turn the metal surface highly selective towards propenol formation. By applying pulsed multi-molecular beam experiments and *in operando* IRAS we identified the chemical nature of the spectator and the reactive surface intermediate as oxopropyl and propenoxy species, respectively. The evolution of the surface concentration of the propenoxy intermediate monitored spectroscopically was found to closely follow the propenol formation rate detected in the gas phase.

In the second part, the catalytic surfaces modified with chiral adsorbates will be discussed. In heterogeneous catalysis, such chiral modification of the non-chiral metal surfaces allows to turn the catalytic processes asymmetric and produce enantiopure compounds. We will discuss the atomistic details of the chiral modification as well as the interaction between the chiral modifiers and the prochiral adsorbates on well-defined Pt(111) surface.

References:

1. Dostert, K.-H. et al, *J. Amer. Chem. Soc.* **2015**, *137*, 13496-13502.

9:20am **HC+SS-WeM-5 In situ Structural Studies and Gas Phase Visualization of Model Catalysts at Work**, *Sara Blomberg*<sup>1</sup>, *J Zetterberg*, *J Zhou*, *J Gustafson*, *E Lundgren*, Lund University, Sweden

Catalysis is widely used in the production process of chemicals, pharmaceuticals, fuels or ammonia synthesis. The catalyst accelerates the chemical reaction but without being consumed. The materials system of a catalyst is complex and as a result, the catalytic process in most cases is not fully understood, and fundamental studies of the catalyst at operating conditions are close to impossible.

In the last decades, a number of *in situ* experimental techniques have been developed operating at semi-realistic condition to extend the fundamental knowledge on catalytic reactions and to bridge the pressure gap. We have therefore used Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) for surface and gas-phase studies and Planar Laser-induced Fluorescence (PLIF) for gas phase visualization.

Using APXPS to investigate the CO oxidation over a Pd(100) single crystal[2], we observe a pressure dependent CO desorption temperature, and therefore a pressure dependent ignition temperature of the reaction. The experiments were carried out by slowly increasing the temperature of the Pd(100) in a 1:1 ratio of CO and O<sub>2</sub> and systematically increasing the total pressure. The increasing ignition temperature of the catalyst is observed in conjunction with an increasing oxygen coverage on the surface measured immediately after the ignition. Remarkably, no CO could be detected neither in the gas phase nor adsorbed on the surface after the ignition of the reaction, despite a highly active surface.

To investigate the gas phase in more detail, we have developed PLIF, where an image of the gas distribution close to the surface is obtained [2]. PLIF was used to study *in situ* the change of the gas phase during CO oxidation,

<sup>1</sup> Heterogeneous Catalysis Graduate Student Presentation Award Finalist

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where the images visualize the build-up of a boundary layer of CO<sub>2</sub> close to the active surface, and the reaction is mass transfer limited by the diffusion of CO. Within this boundary layer the gas composition is significantly different as compare to the composition detected at the outlet of the reactor by a mass spectrometer (MS)[3]. The drastic drop in the CO pressure close to the surface explain the lack of detected CO in the APXPS experiments, which result in a partial pressure of CO below the detection limit of the APXPS.

[1] S. Blomberg et al. In Situ X-Ray Photoelectron Spectroscopy of Model Catalysts: At the Edge of the Gap, *Phys Rev Lett*, **110** (2013) 117601.

[2] Sara Blomberg *et al.* *Phys.: Condens. Matter* **28** (2016) 453002

[3] J. Zetterberg et al. Spatially and temporally resolved gas distributions around heterogeneous catalysts using infrared planar laser-induced fluorescence. , *Nat Commun*, **6** (2015) 7076.

9:40am **HC+SS-WeM-6 Adsorption, Thermal Stability, and Kinetics of Atomic Oxygen at Ag(111) and Ag(110) Surfaces**, *Sara Isbill*<sup>1</sup>, *S Roy*, University of Tennessee Knoxville

Transition-metal surfaces are commonly used to catalyze transformations of small organic compounds, but the catalyst structures and catalytic mechanisms are not yet completely understood. Silver surfaces are important industrial catalysts for the partial oxidation of ethylene to ethylene oxide and methane to methanol. While significant strides have been taken towards revealing the complex chemical pathways of oxidation reactions on silver surfaces, the role of subsurface oxygen (oxygen adsorbed just beneath the surface) in surface reconstruction and oxidative catalysis by silver has yet to be elucidated. In the present study, density functional theory (DFT) was used to probe the interactions of atomic oxygen with the surface and subsurface of Ag(111) and Ag(110) surfaces. The goal was to investigate adsorption, thermal stability, and kinetics of surface and subsurface oxygen at different coverages on the metal surfaces and examine their effects on the structural and catalytic properties of silver. On Ag(111), it was found that both surface and subsurface adsorption energies decreased with oxygen coverage, but surface adsorption weakened more drastically than subsurface adsorption. In contrast, on Ag(110), surface adsorption remained more favorable than subsurface adsorption at all studied coverages. Our thermodynamic and kinetic models of O/Ag(111) based on DFT-computed equilibrium constants and activation energies show that the stability of subsurface oxygen is sensitive to coverage, thereby indicating that the participation of subsurface oxygen in catalysis would strongly depend on coverage. Overall, our results provide valuable qualitative insight into the formation and motion of subsurface oxygen on Ag(111) and Ag(110) surfaces, the importance of metal-adsorbate charge transfer in these systems, and the possible roles of subsurface oxygen in catalytic oxidation by silver.

11:00am **HC+SS-WeM-10 Understanding the Intrinsic Surface Reactivity of Multilayer vs. Single-layer PdO(101) on Pd(100)**, *Jason Weaver*, *V Mehar*, University of Florida; *M Kim*, Ohio State University; *M Shipilin*, Lund University, Sweden; *M van den Bossche*, Chalmers University of Technology, Gothenburg, Sweden; *J Gustafson*, Lund University, Sweden; *L Merte*, Chalmers University of Technology, Gothenburg, Sweden; *U Hejral*, Lund University, Sweden; *H Gronbeck*, Chalmers University of Technology, Gothenburg, Sweden; *E Lundgren*, Lund University, Sweden; *A Asthagiri*, Ohio State University

Understanding the intrinsic reactivity of different types of O-rich phases that form on Pd surfaces is central to developing accurate models of oxidation catalysis. In this talk, I will discuss results of a recent study in which we used temperature programmed reaction spectroscopy (TPRS) and surface IR spectroscopy (RAIRS) as well as DFT calculations to investigate the intrinsic CO oxidation activity of single and multiple-layer PdO(101) structures grown on Pd(100) in UHV. We find that CO binds more strongly on multiple vs. single-layer PdO(101) (~110 vs. 40 kJ/mol), and that CO oxidizes negligibly on single-layer PdO(101) whereas nearly 90% of a saturated layer of CO oxidizes on multiple layer PdO(101) during TPRS experiments. RAIRS further shows that CO molecules adsorb on both bridge and atop-Pd<sub>cus</sub> sites (coordinatively-unsaturated Pd sites) of single-layer PdO(101)/Pd(100), while CO binds exclusively on atop-Pd<sub>cus</sub> sites of multilayer PdO(101). Our DFT calculations reproduce the much stronger binding of CO on multiple layer PdO(101) as well as the observed binding site preferences, and reveal that the stronger binding is entirely responsible for the higher CO oxidation activity of multiple vs. single layer PdO(101)/Pd(100). We show that the underlying O-atom bonding partners,

present only in multiple layer PdO(101), modify the electronic states of the Pd<sub>cus</sub> atoms in a way that enhances the CO-Pd<sub>cus</sub> bonding. Lastly, we show that a simple kinetic model, with energetics determined from the present study, predicts that the intrinsic CO oxidation rates achieved on both single and multilayer PdO(101)/Pd(100) can be expected to exceed the gaseous CO diffusion rate to the surface during steady-state CO oxidation at elevated pressures, even though the intrinsic reaction rates are 4-5 orders of magnitude higher on multiple vs. single layer PdO(101)/Pd(100). Our findings help to resolve seemingly disparate conclusions about the CO oxidation activity of the single and multiple layer PdO(101) structures, as determined from previous *in situ* vs. UHV measurements, and highlight the importance of characterizing the intrinsic reactivity of catalyst surfaces for developing first-principles kinetic models that can accurately reproduce surface reactivity over a wide range of conditions.

11:20am **HC+SS-WeM-11 Simultaneous Study of Catalyst Structure, Gas Phase and Morphology**, *Sebastian Pfaff*, *J Zhou*, *S Albertin*, Lund University, Sweden; *M Shipilin*, Stockholm University, Sweden; *J Gustafson*, *S Blomberg*, *E Lundgren*, *J Zetterberg*, Lund University, Sweden

CO oxidation has long been studied as a model reaction for catalysis diagnosis. In recent time, increased focus has been given to study well-defined single crystal surfaces to further investigate the details of the involved reaction mechanisms[1]. During the past years, new techniques have been developed to study both the surface structure and gas phase in a semi-realistic environment such as High Energy Surface X-Ray Diffraction (HESXRD)[2] and Planer Laser Induced Fluorescence (PLIF)[3]. HESXRD is a technique well suited to gain knowledge about the surface structure, but without any macroscopic spatial resolution. Planar Laser Induced Fluorescence (PLIF) is a technique which excels at determining the structure and composition of the gas phase. One of the main advantages of this technique is its high spatial and immediate temporal resolution. Additionally, LED surface reflectance techniques have been developed, which provide a simple way of producing a macroscopic map of the entire single crystal, clearly visualizing changes on the surface[4].

In this work, the mentioned techniques were combined at the beamline P07 at PETRA III while performing CO oxidation over a Pd(100) single crystal sample. We have shown a clear spatial correlation between a reduced surface reflectance and an increased CO<sub>2</sub> concentration in the gas phase. Additionally, through the sub-second temporal resolution of PLIF, we have determined the delay between a measurable change of the surface structure using HESXRD and a change in gas composition as the catalyst switches between high and low activity.

## References

1. Freund, H.-J., et al., *CO Oxidation as a Prototypical Reaction for Heterogeneous Processes*. *Angewandte Chemie International Edition*, 2011. **50**(43): p. 10064-10094.
2. Gustafson, J., et al., *High-Energy Surface X-ray Diffraction for Fast Surface Structure Determination*. *Science*, 2014. **343**(6172): p. 758-761.
3. Zetterberg, J., et al., *Spatially and temporally resolved gas distributions around heterogeneous catalysts using infrared planar laser-induced fluorescence*. *Nature Communications*, 2015. **6**: p. 7076.
4. Zhou, J., et al., *Simultaneous Imaging of Gas Phase over and Surface Reflectance of a Pd(100) Single Crystal during CO Oxidation*. *The Journal of Physical Chemistry C*, 2017. **121**(42): p. 23511-23519.

11:40am **HC+SS-WeM-12 New Catalysis for Light Alkanes – From Methane Functionalization to Light Akenes**, *Johannes Lercher*, Pacific Northwest National Laboratory and TU München, United States of America/Germany  
**INVITED**

The abundant availability of light alkanes opened new opportunities to synthesize light alkenes and oxygenates, challenged only by the high dispersion of the carbon sources, requiring dedicated processes. Three different principal catalysis pathways will be discussed, the conversion of methane to methanol, the oxidative dehydrogenation of ethane and the dehydrogenation of propane to propene, eventually followed by aromatization. For the three approaches it will be shown, how the atomistic understanding of the catalyst properties including an atomistic description of the active site by combining electron microscopy and X-ray absorption spectroscopy and the molecular pathways by identifying elementary steps via NMR spectroscopy and isotope labeling allows to drastically develop catalysts and catalytic pathways. Combining rigorous kinetics with spectroscopy allowed for all three cases to describe rates linked to specific active sites and maximize their concentration. The

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potential and limitations of this fundamental approaches to discover new catalysts and improve existing will be discussed.

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